

DEPARTMENT OF THE INTERIOR

UNITED STATES BUREAU OF MINES

JOHN W. FINCH, DIRECTOR

INFORMATION CIRCULAR

THE RARE EARTHS



BY

ALICE V. PETAR

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INFORMATION CIRCULAR

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By Alice V. Petar^{2/}

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1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6847."

2/ Rare Metals and Nonmetals Division, U.S. Bureau of Mines.

INTRODUCTION

The rare-earth group are among the least familiar of the 92 known elements. Moreover, the relatively few people who have even heard of the rare earths ordinarily regard them merely as very rare elements having unusual names but doubtful commercial application. This typical attitude can be attributed partly to the fact that no commercial uses have been developed for most of the members of the group and partly to the fact that those which do enter into useful articles do so anonymously. Most people speak with a degree of familiarity of the "chromium" plating on their automobiles or household appliances; "antimony" ash trays and cigarette boxes are on sale in many department stores; and "tungsten" lamps and even "molybdenum" steels are advertised in popular magazines. However, the average user of a pocket cigarette lighter is not conscious that the important sparking element is a "flint" made from ferrocerium, and if he does chance to inquire about the composition he is likely to be told that it is "sparking alloy", "misch metal" or "pyrophoric alloy." Similarly, the wearer of spectacles made of "Crookes" or other tinted glass probably is not aware that the light softening effects are due to the presence of rare-earth oxides, or that the arc light on his street may owe its brilliance to cerium fluoride in the carbon electrode. Despite a variety of practical applications, however, most of the rare-earth metals still must be listed as scientific curiosities. In fact, little is known as to the properties which may make them useful products at some future date. Meanwhile it is important to note that Nature has been relatively generous in her distribution of the rare earths and that adequate supplies of most of them will be forthcoming when these elements have proved their worth as commercial products.

ACKNOWLEDGMENTS

In preparing the present paper abundant use has been made of information contained in an earlier circular, which is now out of print--Bureau of Mines Information Circular 6321, Monazite, Thorium, and Cerium, by R. M. Santmyers. The author has also used extensively J. F. Spencer's *The Metals of the Rare Earths*, J. W. Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (vol. 5), and other works which are acknowledged in footnotes or referred to in the bibliography. Grateful acknowledgment is made of helpful criticism of the manuscript, prior to publication, by Dr. Harlan S. Miner, of the Welsbach Co., Gloucester City, N. J.

DESCRIPTION AND PROPERTIES

In group III of the Periodic Table of the Atoms there appears a single item entitled "Rare Earths" which includes the elements having atomic nos. 57 to 71. The individual elements of this group, in order of increasing atomic weight, are as follows:

Rare-earth elements

Element	Symbol	Atomic No.	Atomic Weight
Lanthanum	La	57	138.92
Cerium	Ce	58	140.13
Praseodymium ..	Pr	59	140.92
Neodymium	Nd	60	144.27
Illinium	Il	61	?
Samarium	Sm	62	150.43
Europium	Eu	63	152.0
Gadolinium	Gd	64	157.3
Terbium	Tb	65	159.2
Dysprosium	Dy	66	162.46
Holmium	Ho	67	163.5
Erbium	Er	68	167.64
Thulium	Tm	69	169.4
Ytterbium	Yb	70	173.04
Lutecium	Lu	71	175.0

Higher up in the same vertical column of the chart but closely related to this group are two other elements, scandium (atomic no. 21) and yttrium (atomic no. 39).

Strictly speaking, the term "rare earths" denotes the oxides, but it is employed conveniently in referring to the elements themselves. The known properties of the individual members of the group are characteristically similar, and ordinarily the elements occur together in the same minerals and are difficult to separate. There are also subgroups or "families"; one arrangement, based on the solubility of the rare-earth oxalates in a saturated solution of potassium sulphate, is as follows:^{3/}

Subgroups of the rare earths^{4/}

Insoluble oxalate (Rare earth)	Insoluble potassium sulphates (cerium family)	{	Lanthanum
			Cerium
	Moderately soluble K sulphates (terbium family)	{	Praseodymium
			Neodymium (Illinium) Samarium
	Readily soluble K sulphates (yttrium family)	{	Europium
			Gadolinium Terbium
	(erbiium family)	{	Dysprosium
			Holmium Erbium Thulium
	(ytterbium family)	{	Yttrium
			Ytterbium
			Lutecium

^{3/} For a simpler arrangement see section on History, p. 8.

^{4/} Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: vol. 5, Longmans & Co., London, 1924, p. 495. (Illinium has been arbitrarily inserted in the "cerium family" because of its position, between neodymium and samarium, in the periodic table.

Considerable literature covers the circumstances of the discovery and gradual refinement of laboratory procedure of these elements, but the details are too technical for inclusion in a general report. The Bureau of Mines has made no special study of the properties of the rare earths; in fact, a large part of the research has been done by European investigators. However, a member of the group, illinium, is one of the few elements discovered in the United States. The following descriptions of the individual rare earths have been abstracted from available literature.

Cerium Family

Members of the cerium family are the only ones of the rare-earth group about which much is known. Except for the recently discovered element 61, illinium, these "earths" have all been employed commercially, either individually or collectively, as "misch metal." The elements in the cerium group are strongly electropositive and are among the most basic of all elements. They are also distinguished from the other rare earths by the fact that they form sparingly soluble double sulphates with sodium and potassium sulphates. The following table summarizes available information with respect to the properties of lanthanum, cerium, praseodymium, neodymium, and samarium.

Properties of elements of cerium family

Element	Atomic Weight	Color	Hardness	Specific	Melting Point, °C.
Lanthanum	138.92	Tin-white	Harder than Ce	6.15	810
Cerium	140.13	Steel-gray	Nearly as soft as lead.	6.9	623
Praseodymium ...	140.92	Yellow	Harder than Nd	6.47	940
Neodymium	144.27	Yellow tinge	Harder than Zn	6.95	840
Samarium	150.43	Pale gray	Hard as steel	7.7-7.8	1,300-1,400

Cerium. - The term "cerium" frequently is used to describe a mixture of the metals of the cerium group having approximately the following composition: Cerium 45 percent, lanthanum 25 percent, neodymium and praseodymium 15 percent, and samarium 10 percent.^{5/} This mixture is employed for a number of purposes where there is no special advantage in separating the individual elements. The following description applies to the element cerium.

Cerium metal resembles steel in appearance; it is lustrous, malleable, very ductile, and soft enough to cut with a knife. It conducts electricity poorly and heat fairly well, and emits sparks when scraped with a file. Cerium is stable in dry air but is oxidized superficially in moist air. It burns more easily than magnesium when heated in air, forming oxide and producing heat and much light. It ignites spontaneously when finely divided and burns in vapors of nitrogen, hydrogen, bromine, iodine, sulphur, and phosphorus.

^{5/} Gillett, H. W., and Mack, E. L., Molybdenum, Cerium, and Related Alloy Steels; Chem. Catalog Co., New York, 1925, p. 89.

forming compounds with these elements. Cold water attacks it slowly and hot water quickly. It is not attacked by cold, concentrated sulphuric acid, or red, fuming nitric acid, and is soluble in dilute sulphuric acid, nitric acid, and dilute or concentrated hydrochloric acid, but insoluble in sodium hydroxide. Cerium forms alloys with many metals and forms both cerous and ceric compounds.^{6/}

Lanthanum. - Lanthanum is a white, malleable, ductile metal, harder than cerium but softer than zinc. The metal takes a high polish, which tarnishes immediately in dry air as it becomes coated with a steel-blue film. Lanthanum burns in chlorine and bromine but less brightly in the latter, and it unites with iodine without producing light. It decomposes slowly in cold water and rapidly in hot water, is soluble in dilute acids, and is attacked easily by cold, concentrated nitric acid but not by cold, concentrated sulphuric acid.^{7/} Owing to the solubility of its salts, lanthanum is the easiest of the rare-earth metals to separate by fractional crystallization. It is the most strongly electropositive rare-earth metal and in its properties is closely related to calcium and magnesium. Lanthanum may be alloyed^{8/} with lead, tin, thallium, magnesium, silver, copper, and gold; most of the alloys are pyrophoric. Investigations at the University of California indicate that lanthanum is slightly radioactive.^{9/}

Praseodymium. - Metallic praseodymium has a faint yellow color and is acted on very slowly by air. It is harder than neodymium but not as hard as samarium. Praseodymium forms two well-defined oxides (Pr_2O_3 and PrO_2), a hydrated peroxide of the formula Pr_2O_5 , and possibly other oxides intermediate between Pr_2O_3 and PrO_2 . Praseodymium salts are greenish and analogous to the cerous and lanthanum salts. Alloys of praseodymium with aluminum and magnesium have been studied by Canneri,^{10/} who found that in properties, including the pyrophoric characteristics, they are similar to the corresponding lanthanum alloys. Praseodymium is closely related to neodymium, and the two elements have many common properties. For some industrial purposes the mixture of the two, didymium, is employed.

Neodymium. - Neodymium is a faintly yellow metal, it is moderately stable in air, although after some hours it becomes covered with a grayish coating of oxide. It is attacked slowly by cold water but rapidly by hot water. Acids dissolve it rapidly, but solutions of alkalis act on it in the same way as pure water.

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- 6/ Segerblom, Wilhelm, Properties of Inorganic Substances: Chem. Catalog Co., New York, 1927, p. 165.
 - 7/ Segerblom, Wilhelm, work cited, p. 173.
 - 8/ Canneri, G., (The Alloys of Lanthanum): Metal. ital., vol. 23, 1931, pp. 802-823. Chem. Abs., vol. 26, no. 4, Feb. 20, 1932, pp. 949-50.
 - 9/ Science News Letter, Three Rare-Earth Elements Proved to be Radioactive: Vol. 23, no. 619, Feb. 18, 1933, p. 99.
 - 10/ Canneri, G., (Alloys of Praseodymium and Aluminum): Alluminio, vol. 2, March-April 1933, pp. 87-89; Metals and Alloys, vol. 5, no. 4, April 1934, p. MA157. (Alloys of Praseodymium and Magnesium): Metal ital., vol. 25, 1933, pp. 250-252; Chem. Abs., vol. 27, no. 21, Nov. 10, 1933, p. 5293.

Neodymium is said to be an almost ideal decolorizing agent in glass, as it produces remarkably little loss of transparency in ultraclear glass. Usual decolorizers absorb much of the light necessary for physiological colorlessness causing the glasses to appear dark.^{11/} According to Prof. R. W. Wood, of Johns Hopkins University,^{12/} rods of quartz, in which a compound of neodymium has been dissolved, when heated give a light from which certain colors are missing; the spectrum is crossed by dark bands. Unlike white-hot incandescent wires such as tungsten filaments, which give a white light that includes all the possible colors, neodymium sends out only special vibrations of its own. Neodymium is said to be radioactive.

Samarium. - Metallic samarium is grayish white and tarnishes in air. It is the hardest of the cerium metals and very brittle. The salts are topaz-yellow. Like lanthanum and neodymium samarium has been found to be radioactive.^{13/}

Illinium. - In 1926 Prof. B. S. Hopkins, of the University of Illinois, announced the discovery of element 61, to which he gave the name illinium.^{14/} Little information is available as to the properties of the element. Professor Hopkins identified it by X-ray spectroscopic means while mapping the arc spectrum line of elements 60 (neodymium) and 62 (samarium). The element was isolated in 1933 by Maurice Curie and M. Takvorian, of the Radium Institute of Paris. No illinium compounds have been reported.

Terbium Family

Published information relative to members of the terbium family is largely historical and is summarized briefly in this report under "History." A recent paper by Hopkins^{16/} on europium states that it is one of the rarest chemical elements. The best estimates now available indicate that it comprises about two millionths of 1 percent of the earth's crust. It has a remarkably persistent spectrum which is easily identified. In consequence, the presence of europium in the sun and some of the fixed stars has been demonstrated. Europium salts form pink solutions. No commercial uses have been suggested for europium or its compounds.

^{11/} Loeffler, Johannes, (Why Neodymium is a Better Physical Decolorizer Than Nickel, Cobalt, Manganese, or Selenium): Sprechsaal, vol. 66, 1933, pp. 629-630.

^{12/} Science News Letter, Rare Element Gives New Kind of Light: Vol. 19, May 2, 1931, p. 276.

^{13/} Science News Letter, Three Rare-Earth Elements Proved to be Radioactive: Vol. 23, no. 619, Feb. 18, 1933, p. 99.

^{14/} For a detailed account of investigations leading to discovery of the element see Hopkins, B. S., Illinium - The New Rare Earth: Jour. Franklin Inst., vol. 204, July 1927, pp. 1-11.

^{15/} Metal Industry (London), Illinium: Vol. 42, no. 16, Apr. 21, 1933, p. 430.

^{16/} Hopkins, B. S., Europium, a Rare Member of the Rare Earth Group: Paper presented at 66th Gen. Meeting of the Electrochem. Soc., Sept. 27 to 29, 1934, Preprint 66-16, pp. 167-174.

Gadolinium and terbium salts form colorless solutions. Known compounds include the bromides, carbonates, chlorides, hydroxides, nitrates, oxides, sulphates, and sulphides. Terbium metal has not been isolated.

Yttrium Family

The yttrium family of the rare earths is made up of two branches - an erbium subgroup and an ytterbium subgroup. All the elements of the erbium subgroup - dysprosium, holmium, erbium, and thulium - were separated from the original erbium (the "terbium" discovered by Mosander in 1843). The metal erbium is described as a dark-gray, metallic powder of specific gravity 4.77 at 15°. It decomposes in water and its salts give rose solutions. Erbium oxide (erbia) is a rose tinted powder, which is infusible and difficultly soluble in warm nitric acid, sulphuric acid, or hydrochloric acid. Its specific gravity is 8.6. The sulphate is soluble in water and has a specific gravity of 3.7. Dysprosium chloride, nitrate, and sulphate are yellow crystalline salts. The oxide is a white powder, soluble in acids, having a specific gravity of 7.8. Holmium oxide (holmia) is a pale-yellow powder, which is insoluble in water but soluble in acids to solutions which produce yellow or orange salts. Thulium oxide (thulia) is a dense white powder with a greenish tinge which when heated glows, first red, then yellow, and finally white. It is slowly soluble in hot, concentrated acids.

The ytterbium subgroup is composed of the elements yttrium, ytterbium, and lutecium. At one time it was believed that an additional element (celtium) belonged to this subgroup. Urbain claimed the discovery of celtium as the result of the fractionation of ytterbium from gadolinite; he also considered that the lines of the spectrum of celtium were in agreement with an element in the periodic table having the atomic number 72. However, the existence of "celtium" as a new element was disproved later, and the credit for the discovery of element 72 (hafnium) went to D. Coster and G. von Hevesy. The atomic number of yttrium (39) is outside the range of numbers of the rare-earth group, but the element is associated intimately with the rare earths in nature and was one of the two original sources from which the rare-earth elements were gradually separated. (This relationship is discussed more fully under "History.") Somewhat impure metallic yttrium has been prepared as an iron-gray powder which is oxidized readily in air and converted into the hydroxide by boiling water. Yttrium is easily soluble in dilute acids; its melting point is 1,490° C. and its boiling point 2,500° C. Its specific gravity is 5.51.

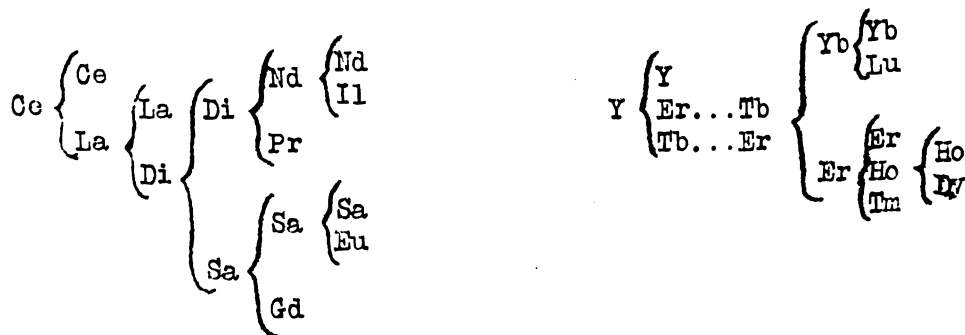
Available information on the properties of ytterbium and lutecium is meager. Solutions of their salts are colorless. Ytterbium oxide (ytterbia) is a heavy, white, infusible powder, slowly soluble in cold acids and easily and rapidly soluble at 100° to colorless solutions. Its specific gravity is 9.2. The sulphate is a white, opaque solid having a specific gravity of 3.8. It is soluble in water and decomposed by heat. The chloride is easily soluble in water, is decomposed to oxychloride by heat, and is soluble in alcohol. The melting point is 150° and the specific gravity 2.6. Lutecium chloride is probably more volatile and more soluble than the ytterbium salt. Its melting point is 916° and its specific gravity 3.9.

Scandium

Scandium, like yttrium, does not belong to the rare-earth group but is linked almost inseparably with elements in the group by association in nature, history, and properties. Scandium is present in many, but not all, rare-earth minerals. According to Urbain and Sarker,^{17/} scandium resembles the rare earths in analytical characteristics, insolubility of fluorides, and slight solubility of oxalates. Other salts of scandium differ widely. Metallic scandium has not been isolated. Additional information will be found in Bureau of Mines Information Circular 6401.^{18/}

HISTORY

The genealogy of the rare-earth family has been traced back to two oxides - yttria, which became known in 1794, and ceria, identified in 1803. The "descendants" of the yttria branch of the family are yttria, terbia, erbia, ytterbia, lutecia, holmia, thulia, and dysprosia, and the ceria group includes ceria, lanthana, neodymia, praseodymia, samaria, gadolinia, europia, and illinia. Diagrams of the rare-earth "family tree" were prepared by the late Prof. Charles James of the University of New Hampshire for the fourteenth edition of the Encyclopedia Britannica, and as they afford a condensed history of the progressive unfolding of our knowledge of the group they are reproduced here:



The following historical summary of the discovery of the rare earths has been abstracted from a paper by Weeks.^{19/}

The Scandinavian Peninsula may well be described as the ancestral home of the rare earths as the first rare-earth mineral was found at Ytterby, a little town near Stockholm, in 1788. In 1794 Jacob Gadolin, a Finnish scientist, discovered in this mineral a new earth, which subsequently was named "yttria."

^{17/} Urbain, G., and Sarker, P. B., The Analogies of Scandium With the Rare Earth Elements and with the Tervalent Elements of the Iron Family: Compt. rend., t. 185, 1927, pp. 593-596; Chem. Abs., vol. 22, 1928, p. 21.

^{18/} Petar, Alice V., Gallium, Germanium, Indium, and Scandium: Inf. Circ. 6401, Bureau of Mines, 1930, 17 pp.

^{19/} Weeks, Mary Elvira, The Discovery of the Elements. XVI. The Rare-Earth Elements: Jour. Chem. Education, vol. 9, 1932, pp. 1751-1773.

The parent mineral was called "gadolinite." In 1803 Klaproth discovered in the mineral cerite another earth, which is now known as "ceria." Two other investigators, Berzelius and Hisinger, who were searching for yttria, also discovered ceria. In 1839 Carl Gustav Mosander found a new earth in ceria which he named "lanthana." In the same year Erdmann discovered lanthana in a new Norwegian mineral, which he named "mosandrite", in honor of Mosander. During the next few years Mosander continued his studies of lanthana and in 1841, after treating it with dilute nitric acid, extracted a new rose oxide which he named "didymium" because it seemed to be "an inseparable twin brother of lanthanum." Didymia was regarded as a pure earth until 1885 when Auer von Welsbach decomposed it. Mosander then turned his attention to yttria in an effort to determine whether it, like ceria, was composed of more than one element. In 1843 he showed that yttria from which all the ceria, lanthana, and didymia have been removed contains at least three other earths. These are a colorless oxide, for which he kept the name "yttria", a yellow earth, erbia, and a rose one, terbia. Other investigators confirmed Mosander's work, but in some way the names "erbia" and "terbia" were interchanged. In 1878 the Swiss chemist Marignac extracted from erbium nitrate two oxides - a red one for which he retained the name "erbia" and a colorless one which he named "ytterbia." The following year Nilson isolated the earth "scandia" from ytterbia.

The erbia left after the removal of ytterbia and scandia was resolved still further by Per Theodor Cleve into three constituents: Erbia, holmia, and thulia. In 1879 Boisbaudran detected the presence of a new oxide in didymia, which he named "samaria." In 1886 he obtained from it still another earth, which proved to be identical with a substance that Marignac had separated from samarskite in 1880. With the consent of the earlier investigator Boisbaudran named this oxide "gadolinia." As previously mentioned Carl Auer von Welsbach in 1885 succeeded in splitting didymia into two earths, for which he proposed the names "praseodymia" and "neodymia." To Baron von Welsbach goes the credit for putting the rare earths to work with his invention of the incandescent gas mantle; as first developed, the mantle fabric was impregnated with a mixture of lanthana and zirconia. His first patent for the Welsbach mantle was dated September 23, 1885. Baron von Welsbach also invented the automatic gas lighter based on a pyrophoric alloy of iron and cerium.

In 1886 Lecoq de Boisbaudran separated pure holmia into two earths, which he called "holmia" and "dysprosia." Europium was discovered in 1901 by Demarcay, as a result of an elaborate series of fractionations of samarium magnesium nitrate. In 1907 Georges Urbain separated ytterbia into two constituents, which are now known as "ytterbia" and "lutecia." Before the news of Urbain's discovery reached America the late Prof. Charles James of the University of New Hampshire had prepared a large amount of very pure lutecia but refrained from pushing his claim for priority of discovery.

The most recent rare-earth element to be discovered is illinium, which was reported by Prof. B. S. Hopkins, of the University of Illinois, in 1926. Shortly after Professor Hopkins' announcement prior claim for the discovery of element 61 was made by Prof. L. Rolla, of the University of Florence. The

latter investigator based his claim on research done a few years previously which he believed indicated the existence of a new element. A description of his work was deposited with the Italian Academy in 1924 in a sealed package, which was brought to light and published after Professor Hopkins' announcement. Professor Rolla proposed the name "florentium" for his discovery. Such controversies have accompanied the discovery of many of the elements, and in this instance writers on both sides of the Atlantic soon expressed their opinions as to the relative merits of illinium and florentium as "contenders" for the position of element 61 in the periodic table. The work of Professor Hopkins and the name "illinium" apparently have been accepted.

OCCURRENCE

That the rare earths are not so scarce as their name implies is stated authoritatively by B. S. Hopkins, discoverer of illinium and recognized authority on the rare earths. He says 20 in part:

The [rare-earth] group as a whole is as abundant in the earth's crust as such useful elements as cobalt, boron, zinc, lead, or arsenic. Indeed, the supply of the single element cerium, the most abundant member of the rare-earth group is probably larger than that of cadmium, tin, mercury, antimony, molybdenum, silver, tungsten, bismuth, gold, or platinum. Indeed, the rarest member of the rare-earth group, the recently discovered element illinium, is probably more than a thousand times as abundant as radium whose commercial importance cannot be denied. As a consequence it may be fairly safe to state that the present limited use of the members of the rare-earth group is due to our lack of information and not to a scarcity of material.

20 Hopkins, B. S., Europium, a Rare Member of the Rare-Earth Group: Paper presented at 66th Gen. Meeting of the Electrochem. Soc., Sept. 27 to 29, 1934. Preprint 66-16, pp. 167-168.

Abundance of rare earths

Atomic no.	Symbol	Percent of rare-earth group ^{1/}	Percent in earth's crust ^{2/}
57	La	7	0.00007
58	Ce	31	.00031
59	Pr	5	.00005
60	Nd	18	.00018
61	Il	<u>3/.02</u>	.0000002
62	Sm	7	.00007
63	Eu	.2	.000002
64	Gd	7	.00007
65	Tb	1	.00001
66	Dy	7	.00007
67	Ho	1.2	.000012
68	Er	6	.00006
69	Tm	1	.00001
70	Yb	7	.00007
71	Lu	<u>1.5</u>	.000015
		99.92	

- 1/ Estimates of Goldschmidt and Thomassen, Geochemical Law of Distribution of the Elements III; Videnskapselskabet's Skrifter I Matemat-Naturv Klasse, no. 5, 1924, p. 49.
- 2/ These estimates are calculated from Dr. H. S. Washington's statement that the entire rare-earth group comprises about 0.001 percent of the earth's crust.
- 3/ This estimate is based on the statement by Dr. G. R. Sherwood that the illinium content of monazite is approximately one tenth that of europium. This ratio undoubtedly does not apply to other rare-earth ores.

RARE-EARTH MINERALS

Dozens of rare-earth minerals are known, but none provides so abundant or economical a source of raw material as monazite. An incomplete list of minerals containing the rare earths follows:

Minerals containing rare earths

Mineral	Composition	Rare-earth content	Occurrence
Aeschynite	Niobate and titanate of the cerium metals	18% ceria; 6% mixed rare earths.	Southern Urals, Norway, and Silesia.
Allanite ...	Silicate of Ca, Al, and Fe with rare-earth oxides Ce, La, Di and Yt.	Ce oxides up to 27%; Yt oxides less than 3%	Colorado, New Jersey., New York, North Carolina, Pennsylvania, Texas, Virginia, and Wyoming, Massachusetts, Connecticut; Canada, Greenland, Scotland, Norway, Silesia.

Minerals containing rare earths-Cont'd

Mineral	Composition	Rare-earth content	Occurrence
Cappolenite	Borosilicate of yttrium and barium, with small quantities of Ce, La, and Th oxides.	57% mixed rare earths.	Found sparingly on Lille Arø, southern Norway
Cenosite ...	Hydrous calcium-yttrium silicate and carbonate.	37% yttrium oxides	Island of Hitterø, Norway.
Cerite	Silicate of cerium-group metals with Fe and Ca.	50-70% ceria	Colorado and Bastnäs, Sweden.
Delorenzite	Complex titanate of rare earths.	14% yttria	Craveggia, Italy.
Eucolite Eudialyte	Complex silicate of rare-earth metals with Ca, Fe, and high percentage of ZrO ₂ .	5% mixed rare-earth oxides.	Arkansas; Greenland, Norway.
Euxenite ...	Niobate and titanate of Yt, Er, Ce, and U.	13-27% yttria; 3-9% erbia; 2-8% ceria	Jølster, Norway.
Fergusonite	Metaniobate and tantalate of Yt with Ce, U, etc.	18-26% yttria; 3-13% erbia; 1-9% ceria.	Massachusetts, North Carolina, Texas, Virginia; Australia.
Gadolinite .	Basal orthosilicate, chiefly BeO, iron protoxide, and yttrium oxides.	51% rare-earth oxides.	Arizona, Colorado, Texas; Norway and Sweden.
Lanthanite .	Hydrous lanthanum carbonate.	52.4% lanthanum trioxide.	New York, Pennsylvania, Sweden.
Monazite ...	Phosphate of the cerium metals.	See analyses, pp. 14, 15 and 17.	Arizona, California, Colorado, Connecticut, Florida, Indiana, Montana, Nevada, New Mexico, Oregon, South Dakota, Texas, Utah, Virginia, Washington, Wyoming; Australia, Brazil, Ceylon, China, India, Japan, Madagascar, Norway.
Parisite ...	Fluocarbonate of the cerium metals.	37% Ce, 6% La, 8% Di	Colombia, Norway.
Polycrase ..	Niobate and titanate of Yt, Er, Ce, and U.	13-27% yttria; 6-8% erbia; 2-3% ceria.	North and South Carolina, Texas; Norway, Sweden.
Samarskite .	Niobate and tantalate of Fe and Ca with Ce and Yt metals and uranium oxide.	6-15% yttria; 2-6% ceria,	North Carolina, New Mexico; Canada, India, U.S.S.R., Brazil.

Minerals containing rare earths-Cont'd

Mineral	Composition	Rare-earth content	Occurrence
Rowlandite	Yttrium silicate	51% yttria	Llano County, Texas.
Xenotime ...	Yttrium phosphate	do	Georgia, North Carolina, Colorado; Norway, Sweden, Switzerland, Brazil.
Yttrialite	Silicate of thorium and yttrium oxides.	46% yttria	Llano County, Tex.
Yttrocerite	Fluoride of Ca with metals of Ce and Yt groups.	14% yttria and 9% ceria.	New York, Maine.
Yttro-tantalite	Tantalate and niobate of Fe, Ca, and oxides of Yt, Er, Ce, and U.	10-19% yttria; 6% erbia; and 2% ceria.	Ytterby, Sweden.

Monazite

Monazite is virtually the only commercial "ore" of the rare earths. It has been valued chiefly for its thoria content, which in high-grade commercial material may range from 6 to 9 percent, but ceria, lanthana, neodymia, praseodymia, and other rare earths are present in substantial percentages.

In minor quantities monazite is distributed widely in igneous rocks throughout the world, especially in gneisses that have been intruded by pegmatites, but usually it forms only a very small fraction of 1 percent of the containing rock, and only the natural concentrations in stream gravels and beach sands have paid for exploitation. The commercial deposits of monazite, like placer-gold deposits, are the result of decomposition of the rocks containing the mineral. Monazite, like gold, is not readily attacked chemically by the agencies of erosion, and as it is much heavier than most of the other products of rock degeneration it is concentrated gradually by stream and wave action. River waters will effect a concentration of the heavy minerals, which may gradually be carried to the ocean to be reconcentrated in beaches. Likewise, if the ocean encroaches upon an area of monazite-bearing sands, a still further concentration will take place. Seacoast deposits of sand contain a higher percentage of monazite and cover larger areas than known river-bed deposits. The leading commercial sources of monazite sand are beach deposits in Brazil and India.

United States. - The most important domestic deposits of monazite are in the Carolinas, Idaho, and Florida. The Carolina deposits are in an area in the central part of western North Carolina and northwestern South Carolina, comprising about 3,500 square miles and including all or parts of Alexander, Iredell, Caldwell, Catawba, Burke, McDowell, Gaston, Lincoln, Cleveland, Rutherford, and Polk Counties in North Carolina and Cherokee, Laurens, Spartanburg, Greenville, Pickens, Anderson, and Oconee Counties in South Carolina. The Idaho deposits are near Centerville, in the Boise Basin. Monazite is associated with zircon and ilmenite in beach sands at Mineral City, Fla., 4 miles south of Jacksonville Beach. Elsewhere in the United States occurrences of monazite have been reported at various localities in California, Colorado, Connecticut, Indiana, Montana, Nevada, New Mexico, Oregon, South Dakota, Texas, Utah, Virginia, Washington, and Wyoming. Analyses of Carolina monazite follow:^{21/}

Analyses of samples of monazite from the United States

	1	2	3	4	5	6	7
ThO ₂	6.49	1.48	1.22	1.43	2.32	1.19	7.00
Ce ₂ O ₃	31.38	37.26	54.03	32.93	65.32	61.77	34.50
(La, Di, Yt) ₂ O ₃ .	30.88	31.60		25.54			28.80
P ₂ O ₅	29.28	29.32	23.43	18.38	28.16	26.05	26.00
SiO ₂	1.40	.32	1.60	6.40	3.20	1.45	2.00
ZrO ₂			3.25				.70
TiO ₂				4.67	.61	1.40	.90
Fe ₂ O ₃			5.58	7.83		.65	
Al ₂ O ₃			2.49	1.62		.15	
CaO				1.20			.70
H ₂ O	.20	.17					
Miscellaneous .			3/7.74			4/6.39	
	99.63	100.15	99.34	100.00	99.61	99.05	100.20

1/ Including ZrO₂ and BeO.

2/ Including ZrO₂, BeO, and Ta₂O₅.

3/ Including 4.12 percent (Cb, Ta)₂O₅ and 3.62 percent FeO.

4/ Ta₂O₅.

Brazil. - Monazite sand deposits in Brazil include: (1) The beach deposits reserved to the Government; (2) beach deposits lying behind Government reservations; and (3) inland deposits. The bulk of the monazite produced in Brazil is derived from coastal sands in the States of Bahia and Espirito Santo. These beach deposits are the property of the Federal Government for 33 meters inland, measured from the point where the sea waves wash the beach at mean high tide, but this method of marking property is uncertain and has, of course, caused boundary disputes.

^{21/} Schaller, W. T., Thorium, Zirconium and Rare-Earth Minerals in 1919: U.S. Geol. Survey Mineral Resources of the United States, pt. II, 1919, p. 12.

At a few places along the coast strips of monazite-bearing sands lie directly behind, but not far from, the Government land; these might be worked profitably, but it has been difficult to prove that these sands were not taken from nearby Government land. Along the banks of large rivers, such as the Parahyba, are great quantities of black sands with traces of monazite. Such deposits have been worked near Sapucaia. Many of the inland deposits cannot be exploited on account of the expense of transportation of the products, as the deposits are many miles from the railroads. Analyses of monazite from Brazil are shown in the following table:^{22/}

Analyses of samples of monazite from Brazil

	1	2	3	4	5	6
ThO ₂	9.23	10.05	1.09	6.06	6.50	6.49
Ce ₂ O ₃	31.21	32.14	32.46	62.92	62.10	31.28
(La,Di) ₂ O ₃ ..		25.99	36.02			
P ₂ O ₅	28.36	25.51	29.18	28.50	28.46	29.28
SiO ₂	10.14	2.63		.75	.64	1.40
ZrO ₂	5.74	.60				
TiO ₂	2.62					
Fe ₂ O ₃	4.22	1.79	.61	.97	1.50	
Al ₂ O ₃	.32	.84		.10	.08	
CaO	1.11	.20	.10	.21	.30	
H ₂ O		.92		.38	.64	.20
Ta ₂ O ₅	1.16					
	94.11	100.67	99.46	99.89	100.22	99.53

- 1/ Monazite from river bed, in large pieces weighing as much as 2 pounds; derived from pegmatite Southern Serra dos Amares, Espirito Santo. Freise, F., Ztschr. prakt. Geol., vol. 18, 1910, pp. 123-124.
- 2/ From river sands of Rio Paraguassir in Bahia, Bandeiro do Mello. Hussak, E., and Reitingen, J., Ztschr. Kryst. Min., vol. 37, pp. 550-579, 1903.
- 3/ Sand from Bandeirinha, near Diamantina, Mines Geraes. Idem.
- 4/ Espirito Santo. Johnstone, S. J., Jour. Soc. Chem. Ind., vol. 33, 1914, pp. 55-59.
- 5/ Alcobaca, Borhia. Idem.
- 6/ Brazilian monazite. Analysis furnished by F. H. Lee. Gottschalk, A.L.M., Min. and Eng. World, May 15, 1915.

India.^{23/} - Deposits of monazite sand especially rich in thorium were discovered in 1909 along the sea coast in the State of Travancore in the extreme southwestern part of India. Many of the soils and river sands show monazite,

^{22/} Schaller, W. T., work cited, p. 12.

^{23/} Schaller, W. T., Thorium, Zirconium, and Rare-Earth Minerals in 1919: U.S. Geol. Survey Mineral Resources of the United States, pt. II, 1919, pp. 8-9.

but only certain naturally concentrated deposits along the seacoast are of workable extent. Although there are numerous patches of beach monazite sand in Travancore, only four now are considered of commercial size. The first deposit is on the east coast, about 3 miles north of Cape Comorin. The sand is very fine, and the monazite content is sometimes as high as 20 percent, although the average is much less, depending on wave action. Farther south and immediately north of the cape is the second deposit, much more extensive but of the same general character. The potential yield of these two deposits, together with the periodical accretion due to the action of the waves, is estimated at several thousand tons of commercial monazite.

The third deposit, by far the richest, is on the west coast, immediately north of Cape Comorin. The extreme southern portion is very rich in monazite, reaching 50 percent or more. It has been estimated that 1,200 tons of monazite could be produced annually from this deposit for 20 years.

The fourth deposit is on the west coast about 8 miles south of Trevandrum, the capital of the State, and is not quite as rich as the other three. Numerous other patches which may be of economic importance are interspersed in the regions between these four major fields.

Monazite occurs also in beach sands at Satvaya, on the Orissa coast.^{24/} In January 1924 the Department of Geological Survey of India undertook a survey of the area, which revealed that the deposits were about 23 miles long, 70 feet wide, and 10 inches thick. The average content of monazite in the sand ranges from 2 to 3 percent (richest sample, 11 percent), compared with the Travancore sands which average 10 percent monazite (richest sample, 60 percent). The thoria content is 7.9 percent compared with 8 to 10 percent for Travancore monazite. Ilmenite is also present in the sand.

Ceylon. - Ceylon is a minor commercial source of monazite. Immediately preceding the World War the Ceylon Government Mining Survey found substantial deposits of monazite sand near Bentota and near Kudremalai on the west coast of Ceylon. Samples of the Bentota sand contained as much as 47 percent monazite and over 4 percent thoria; by concentrating these electromagnetically to eliminate the ilmenite and zircon, a very high grade of monazite can be obtained containing nearly 10 percent of thoria.

Analyses of monazite from India and Ceylon are shown in the following table:^{25/}

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- ^{24/} Roy, S. B., Occurrence and Industrial Possibilities of Monazite in the Black Sands on the Orissa Coast: Chem. and Ind., vol. 52, no. 37, Sept. 15, 1933, p. 745.
- ^{25/} Schaller, W. T., work cited, p. 13.

Analyses of samples of monazite from India and Ceylon

	1	2	3	4	5	6
ThO ₂	10.22	3.65	10.75	10.29	9.49	7.90
Ce ₂ O ₃	31.90	61.73	26.71	27.37	27.15	56.50
(La, Di) ₂ O ₃	28.46		31.52	32.27	33.52	
P ₂ O ₅	26.82	26.50	24.61	27.67	26.12	26.80
SiO ₂	.90	1.00	2.47	1.03	1.67	1.92
Fe ₂ O ₃	1.50	1.09	1.09	.81	.87	1.40
Al ₂ O ₃	.17	.12	.70	.17	.17	.13
CaO	.20	.13	.85	.41	.45	.27
H ₂ O	.46	.45	.93	.20	.48	2.20
U ₃ O ₈						2.66
	100.63	99.67	99.63	100.22	99.92	99.78

- 1/ Sand from Travancore, India.
- 2/ Isolated from a concentrate from Travancore, India.
- 3/ From sand from Niriellaganga, Ceylon.
- 4/ Monazite pebble from Ratnapura, Ceylon.
- 5/ Monazite pebble from Muladiwanella Durayakanda, Gilimale, Ceylon.
- 6/ Washed from pegmatite containing 100 grams monazite per metric ton (0.01 percent) from Rifle Range Stream, Moon Plains, Ceylon.

Africa. - Monazite occurs with ilmenite and zircon in beach sands on the coast of Senegal south of Dakar, French West Africa. A deposit of possible commercial size but containing only 4 percent thorium has been reported about 60 miles northeast of Pretoria, and monazite and other rare-earth minerals are said to occur in Swaziland.

Australia. - Certain alluvial deposits in Western Australia^{26/} contain monazite, cassiterite, and the rare-earth minerals fergusonite, euxenite, and gadolinite. The monazite from Cooglegong is in small pebbles averaging about one fiftieth ounce in weight. A sample of the sand from this district contained 80 percent monazite and yielded 3.46 percent thorium. The monazite sand from the residue obtained by resluicing low-grade alluvial tin ore contained 26 percent monazite. The individual pebbles of monazite yielded a little more than 5 percent thorium.

In South Australia, monazite and fergusonite are present in holdings of the Mount Painter radium field a few miles from Copley and are mined for their radioactive content.

Monazite of low thorium content (0.35 to 4.12 percent) is a frequent associate of tin and tungsten deposits in the New England region, New South Wales. It is also present in beach sands at Coolangatta and Currumbin, in Queensland, and on the west coast of Tasmania, in the vicinity of the Stanley River.

^{26/} Schaller, W. T., work cited, p. 10.

Norway. - The pegmatites of southern Norway contain large crystals and masses of monazite, which are saved by the feldspar miners and sold as a byproduct. It is reported, however, that the quantity so obtained and sold has never been more than 1 ton for any year.

Monazite has been reported at various localities in Burma; in the Pointe du Bois region, Manitoba, Canada; and in pegmatites at Ishikawa, Iwaki Province, Japan.

Allanite

Next to monazite allanite is the most abundant cerium mineral. It belongs to the epidote group and occurs as an accessory constituent in granite, syenite, diorite, gneiss, limestone, etc. In the United States deposits are known in Colorado, New Jersey, New York, North Carolina, Pennsylvania, Texas, Virginia and Wyoming. Although most of these are of mineralogical interest only, commercial shipments have been made from Wyoming, Virginia, and possibly North Carolina. Allanite is said to occur in rather large amount at Franklin Furnace, N. J., in the granite dike that pierces the ore body of the Trotter mine, and in pegmatitic masses in abandoned iron mines in the vicinity.^{27/} An interesting occurrence at Baringer Hill, Tex., has been described by Hess.^{28/}

Cerite

Cerite is the richest known cerium-bearing mineral; the ideal mineral contains 50.7 to 71.8 percent cerium. It was named in honor of the discovery of the minor planet Ceres in 1801.

In the United States cerite has been found in Boulder County, Colo., near Jamestown, but so far as is known only specimen material has been obtained. The best-known occurrences of cerite are in the Bastnäs mines in the Rydhyttan district, Sweden. It was there that cerite was first discovered, and 4,400 metric tons of high-grade cerium ore were mined between 1875 and 1888.^{29/}

Gadolinite

Gadolinite is of interest as a rare-earth mineral because of its yttria content, which, however, sometimes is partly replaced by the oxides of cerium, lanthanum, and didymium. Small quantities of thorium are also present sometimes. Gadolinite usually is found in pegmatites and frequently is associated with allanite and other rare-earth minerals. The earliest discovery of the

^{27/} Kemp, J. F., The Granite at Mounts Adam and Eve, Warwick, Orange Co., N.Y. and Its Contact Phenomena: New York Academy of Sciences, vol. 7, 1892-94, pp. 638-50.

^{28/} Hess, Frank L., Minerals of the Rare-Earth Metals at Baringer Hill, Llano County, Texas: U.S. Geol. Surv. Bull. 340 (d), 1907, pp. 286-294.

^{29/} Geijer, Per, The Cerium Minerals of Bastnäs at Riddarhyttan: Sveriges Geologiska Undersökning Årsbok, vol. 14, no. 6, 1920, 24 pp.

mineral in the United States was at Devil's Head Mountain, Douglas County, Colo.; it has also been found in considerable quantity in pegmatites in Aquarius Cliffs, Mohave County, Ariz. The principal domestic source, however, is at Baringer Hill, Llano County, Tex. A double crystal of gadolinite weighing 73 pounds was found there in 1903 when the deposit was being worked by the Nernst Lamp Co., Pittsburgh, Pa.

CHEMICAL SEPARATION

The rare earths are so similar in properties that they tend to enter into similar chemical reactions. The first problem, of course, is to get the mineral into solution. Most of the rare-earth minerals are not readily soluble and accordingly must be powdered very finely. Digestion with hot hydrochloric acid or with hot concentrated sulphuric acid frequently will effect solution, but some minerals require fusion with acid sodium sulphate or digestion with hydrofluoric acid. According to Spencer:^{30/}

The minerals cerite, orthite, gadolinite, thorite, and yttrialite yield readily to treatment with hydrochloric acid. Xenotime, yttrotitanite, thorianite, and monazite require sulphuric acid for their decomposition, whilst fergusonite, euxenite, polycrase, samarskite, and yttrotantalite can only be got into solution by fusion with sodium bisulphate or treatment with hydrofluoric acid. It is always wiser when a mineral has to be fused to use sodium bisulphate in preference to potassium bisulphate, because many of the rare-earth sulphates form sparingly soluble double sulphates with potassium sulphate, whereas those that they form with sodium sulphate are much more soluble. When a mineral is digested with hydrofluoric acid, the rare earths are left as insoluble fluorides which must be decomposed by boiling with sulphuric acid in order to obtain a solution.

A scheme for the qualitative separation of the rare earths, starting with a chloride solution which is treated with sodium sulphate, was worked out by Prof. Alfred James and is reproduced in J. F. Spencer's *The Metals of the Rare Earths*. Some individual chemical characteristics are mentioned in the foregoing descriptions of the elements themselves. In general, however, the separation of the rare earths from each other is tedious and often has to be done repeatedly to remove traces of a residual element. There are two principles of separation, depending upon (1) the variations in basicity and (2) the varying degree of solubility of the different salts in water and other solvents. As the basicity of the rare earths varies from element to element, fractional precipitation of the hydroxides and fractional decomposition by heat of decomposable salts (for example, nitrates) may be utilized. Fractional crystallization of the various salts has been the subject of much careful study, the extent of which perhaps is indicated by the list of compounds that have been suitable for specific separations; this list includes the sulphates, nitrates, oxalates, formates, acetates, ethyl sulphates, and bromates; double nitrates with ammonium, magnesium, bismuth, manganese, or nickel; double sulphates with the alkali metals; acetylacetonates; dimethyl phosphates; and picrates.

^{30/} Spencer, J. F., *The Metals of the Rare Earths*: Longmans, Green & Co., London, 1919, p. 22.

USES

Many industrial outlets for the rare earths do not require separation of the individual elements, and for such purposes a rare-earth mixture is employed. This is true in some of the more important fields, such as pyrophoric alloys, flaming-arc carbons, and textile treatment. Some specialized uses, such as the glass industry, pharmaceuticals, etc., require pure cerium, neodymium, or praseodymium compounds. At present "cerium", which usually means the mixture of metals in the rare-earth group, is the principal article of commerce; neodymium and praseodymium are used to some extent for optical glass and art glassware, and 1 or 2 minor uses for lanthanum have been developed. For the other individual members of the group, however, there are no important commercial outlets. The first industrial use for cerium was in gas-mantle manufacture. This is still an important consuming industry, although the percentage of cerium nitrate (1 percent) employed is so small that the actual quantity consumed is not impressive.

Pyrophoric alloys

The leading use for the cerium metals is in the manufacture of pyrophoric alloys, but no figures are available as to the amount consumed in this field. Welsbach, in his research on the rare-earth metals, discovered in 1903 that certain alloys when scratched with a file gave off sparks capable of igniting inflammable gas. Later discoveries and improvements demonstrated that an alloy of cerium metals with iron has the maximum pyrophoric properties.

This alloy, known as "sparking alloy", "misch metal", "ferrocium", or "pyrophoric alloy", is used in automatic gas-lighting devices, miners' safety lamps, and cigar and cigarette lighters. It was used to a limited extent during the war in star shells, tracer bullets (the friction with the air causing it to flame brightly), and automatic lighters for use in trenches and other places where matches proved impracticable.

Method of manufacture. - The pyrophoric alloys may be made either from metallic cerium or from a mixture of the cerium-earth metals in approximately the following proportions: Cerium, 50 to 75 percent; lanthanum, neodymium, and praseodymium, 25 to 45 percent; and iron, 0.5 to 1 percent.^{31/}

In the manufacture of pyrophoric alloys the rare-earth residues obtained as a byproduct from monazite sand first are converted to the anhydrous chlorides. The complete dehydration, which is a rather difficult process, is essential in preparing the material for the subsequent steps in its manufacture. The first step is to prepare the material for electrolysis; it has been found that to do this suitably for the continuous commercial production of metallic cerium certain special precautions are necessary. Rather limited ranges of temperature are required for performing efficiently the two processes carried out in the electrolytic cell; these are called, respectively, "separating

^{31/} United States Tariff Commission, Incandescent Gas-Mantle Industry: Tariff Inf. Surveys C-22, 1921, p. 27.

temperature" and "agglomerating temperature." The electrolyte is prepared preferably by using a solution of a mixture of chlorides of cerium and other rare-earth metals of which cerium is the chief constituent. It should be comparatively free from sulphuric acid and sulphate.^{32/}

The purity of this solution is not important, except for the percentages of sulphur and phosphorus compounds and for certain bases such as iron and aluminum compounds, which should be reduced below 3 percent. An excess of cerium oxide will precipitate the iron and aluminum, and calcium chloride (or better, barium chloride) will throw down the sulphates and phosphates.

The solution is then clarified by filtering it hot or settling it, and evaporated to dryness. The preparation of the electrolyte should be carried out so as to obtain the proper surface-tension conditions between the fused electrolyte and the fused metal in the electrolytic bath. An excess of certain impurities, including oxychloride, tends to reduce the surface tension between the metal and electrolyte in the bath and to alter the viscosity, producing an emulsion or colloidal solution of metal in the electrolyte and preventing separation of the metal from the bath.

The electrolysis is done in pots of cast iron high in carbon and silicon, about 8 inches in diameter, and 12 to 18 inches in depth, usually set in brickwork. The heat is applied externally and almost wholly at the bottom of the pot. A small amount of the electrolyte is first put into the pot and nearly fused by a gas heater. The electric current is then turned on and the fusion completed. More electrolyte is added gradually, the contents being brought to the fusion point each time, until the pot is full. Either carbon or graphite anodes are used.

When the mixture of metals comes from the pot, it is relatively soft and does not spark easily upon scratching. To make the commercial product, therefore, it is alloyed with about 30 percent of other metals, chiefly iron, and formed into small pieces to make the "flints" used in lighters, etc. The alloy enters into commerce in the form of small sticks or rods, either rectangular or round, and of various lengths, ranging from 200 to 2,000 pieces per pound. Probably the commonest form is a round piece approximately one-eighth inch in diameter and one-eighth inch long; it takes 1,500 to 2,000 pieces of this size to weigh 1 pound.

The manufacture of these small pieces from "misch metal" is difficult and requires delicate and expensive equipment.

Flaming-arc Carbons

Cerium, in the form of the fluoride, is also used extensively in carbons of arc-lamp electrodes. The flaming-arc electric lamp is based on the principle of introducing oxides of rare-earth metals into the carbons to secure an increased flame arc, somewhat as the Welsbach gas mantles increase the luminosity of a gas flame.

^{32/} Hirsch, Alcan, The American Pyrophoric Alloy Industry; Chem. and Met. Eng., vol. 19, no. 62, Sept. 18, 1918, pp. 510-511.

Calcium chloride and the oxides of iron, titanium, chromium, etc., were first employed with more or less success. To make the carbons (which are commonly of petroleum coke, ground fine and mixed with tar, forced through dies and dried), the metallic oxides either are mixed with the mass or introduced as a core into the center of the carbon. An increased voltage is required, as the electrodes are drawn farther apart to get a long flame. In some forms, as the magnetite lamp, the lower (positive) electrode is simply a permanent knob of copper, while the upper (negative) electrode carries the mineral salts. Such lamps give a large body of arc or flame and do not burn a crater in the carbon but consume a comparatively flat surface when directly opposed. In one form two carbons are employed, positioned like the sides of a V. The quantity of vapor given off by the flame-arc lamps necessitated an open globe at first, but later it was found possible to draw out the vapor by a draft and enclose the carbons in a suitable glass globe.

Glowing Lamps

Before the tungsten filament lamp was introduced the rare-earth metals were used in the Nernst lamp. Instead of carbons it employed what is known as a "glower", - a little rod something over an inch long made principally of the oxide of zirconium, with varying amounts of rare-earth oxides, such as yttria, erbia, thorium, and ceria, mixed with a binding paste and baked into a material resembling porcelain. This rod was provided with platinum terminals. When a current was passed through it, it emitted a soft white light. The life of this form of lamp was 400 to 600 hours; thus it outlasted the arc-lamp carbons, which have a life of only 80 to 175 hours before they have to be replaced.

Incandescent Gas Mantles

One of the earliest commercial uses for the rare earths was in the manufacture of incandescent gas mantles. After several years' study of the rare-earth elements Dr. Carl Auer von Welsbach in 1884 patented the use of a fibrous network composed of the oxides of certain rare-earth metals as a lighting medium. At one time lanthana, zirconia, and ceria were employed for this purpose, but further research revealed the desirability of using a mixture of approximately 99 percent thorium nitrate and 1 percent cerium nitrate. This development (1893) and the subsequent discovery of sufficiently large deposits of the raw material (monazite) gave impetus to an industry which assumed large proportions while electricity was replacing gas in the lighting of homes, offices, factories, and streets. About 1900 a further improvement was made in the form of the inverted mantle, which throws the light downward instead of upward, thereby preventing a shadow.

Method of manufacture. - The gas mantle generally is woven of cotton, ramie or artificial silk fiber into the form of a hose or tube, bleached, and washed very thoroughly in distilled water to decrease the quantity of mineral matter and to remove grease and other foreign substances.^{33/} After drying in a current

^{33/} U.S. Tariff Commission, Incandescent Gas Mantle Industry: Tariff Information Survey C-22, 1921, p. 21.

of hot air the fabric is then treated with the "rare-earth" nitrates - a solution containing 25 to 50 percent thorium and cerium nitrate in the proportion of about 93 to 99 parts thorium nitrate to 1 to 2 parts cerium nitrate. Small quantities of beryllium nitrate and magnesium nitrate also are added to the solution to strengthen the ash skeleton. The fabric is then cut into suitable lengths and one end closed and sewed with asbestos thread. After this the mantle is "fixed", a process which strengthens the parts of the mantle subjected to the greatest strain and is accomplished by treating these parts with a thorium solution containing considerable alumina and alkaline earths. If desired, the mantle may then be branded with the manufacturer's trade mark by the use of a mixture containing didymium nitrate, a byproduct of the manufacture of cerium nitrate. After the fabric is dried and shaped it is "burned off", and the nitrates are converted into the oxides by an intense flame. The mantles that are not damaged in heating and have passed inspection for size, shape, and material defects are dipped into a solution of collodion to give them the strength necessary to withstand the shocks of shipping.

The rare-earth nitrates may be replaced in the fixing process by the corresponding acetates or formates, and if of artificial silk the impregnated stocking is treated with ammonia or some volatile alkali such as hydrazine or tetraethyl ammonium hydroxide to produce the hydroxides of thorium and cerium within the fibers. Hydrogen peroxide may also be employed as the precipitant.

Although the optimum effect usually is attained by mixing the thorium and cerium salts in such proportions that the mixed oxides of the mantle consist of 98.8 percent thoria and 1.2 percent ceria, it is customary, owing to the yellow color of the light produced by this amount of ceria in inverted mantles, to reduce the proportion of ceria to 0.5 to 0.7 percent.

Mixtures of ceria and thoria have a catalytic action on the combination of hydrogen and oxygen which reaches a maximum at 450° C. when the mixtures contain 1 percent of ceria. This was the mixture finally used by Welsbach to obtain the highest illuminating power. The activity or, in other words, the illuminating power of pure thoria is the same as that of a mixture containing 9 percent ceria.

It has been considered that the Welsbach mixture represents the best illuminant obtainable from the two oxides thoria and ceria.

Gas-mantle Industry. - Only within recent years have figures become available with respect to sales of incandescent mantles in the United States. Various estimates have been made from time to time which indicate that immediately before the World War the United States consumed approximately 60 million mantles, subsequently decreasing by approximately 50 percent. According to the Bureau of the Census, domestic production of incandescent mantles was valued at \$1,595,978 in 1929, \$1,135,359 in 1931, and \$686,334 in 1933.^{34/} Imports and exports of incandescent mantles are shown in the following tables.

^{34/} 1933 value (preliminary) is not strictly comparable with figures for earlier years, as a different schedule was used.

TABLE I. - Incandescent mantles imported for consumption in the United States, 1918-34^{1/}

Year	Dozens	Value	Year	Dozens	Value
1918	260	\$ 316	1927	88,840	\$24,947
1919	11	54	1928	72,166	19,769
1920	17,375	13,243	1929	90,892	25,054
1921	51,830	27,001	1930	49,026	15,042
1922	200,659	92,713	1931	18,156	5,270
1923	172,261	65,816	1932	- - -	- - -
1924	171,750	54,507	1933	- - -	- - -
1925	215,404	60,980	1934	54	143
1926	138,748	43,408			

^{1/} Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation of the United States.

TABLE 2. - Domestic exports of incandescent mantles, 1918-34^{1/}

Year	Value					Total	
	Canada	British India	Hong Kong	Australia	All other	Quantity ^{2/}	Value
1918	\$90,246	\$22,043	\$7,874	\$10,726	\$121,395		\$352,284
1919	70,654	31,073	6,817	23,308	226,790		358,642
1920	78,359	74,404	16,342	58,125	251,141	<u>Pounds</u>	478,371
1921	89,599	46,791	2,394	7,538	57,942		204,264
1922	53,155	50,787	925	10,917	49,160	139,640	164,944
1923	42,313	48,277	6,610	10,534	39,102	120,546	146,836
						<u>Dozens</u>	
1924	39,805	47,814	6,603	11,818	48,264	186,928	154,304
1925	35,283	42,946	6,486	18,939	52,239	199,979	155,893
1926	30,401	40,275	5,839	30,149	73,114	230,671	179,773
1927	28,904	46,016	8,405	8,527	53,324	201,890	145,176
1928	36,322	34,849	8,390	26,872	95,842	240,910	202,275
1929	41,828	54,425	12,241	21,902	116,277	316,994	246,673
1930	24,039	30,339	8,736	26,925	89,691	224,237	179,730
1931	26,021	24,963	12,605	16,831	68,036	189,440	148,456
1932	27,798	18,877	6,647	3,991	57,358	144,049	114,671
1933	29,609	13,449	1,395	41	129,489	104,056	84,995
1934						3/117,433	92,140

^{1/} Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation of the United States.

^{2/} Not available prior to 1922

^{3/} Subject to revision.

Gas-mantle scrap. - In the manufacture of incandescent gas mantles the converting of the thorium and cerium nitrates into oxides by a process known as "burning off" requires considerable skill. From 2 to 3 percent of the upright mantles and 10 to 20 percent of the inverted mantles are damaged in the process. These mantles, together with worn-out mantles collected from gas companies and other large consumers, carry considerable thorium and cerium salts. They are reduced to ashes by a firing process, and the ashes are treated further for the recovery of the valuable thorium and cerium oxides. Prior to the World War the United States imported several thousand dollars worth of gas-mantle scrap annually, but subsequently this source of rare-earth residues has dwindled to insignificant proportions. Except for 30 pounds of scrap valued at \$10, imported in 1929, no importations of this material have been recorded since 1922.

Glass Industry

In recent years there has been an increasing trend toward the use of rare-earth compounds in glassware. Cerium is particularly effective in absorbing ultraviolet rays and is employed, either alone or with didymium (neodymium and praseodymium), in spectacle lenses of the Crookes glass or Cruxite type. Didymium itself is not an efficient combination for cutting ultraviolet rays and is present only because of the high cost of didymium-free cerium. However, it does absorb the yellow part of the spectrum and is used commercially in lenses of glassblowers' goggles. It is claimed that didymium glass entirely shuts off the blinding yellow rays produced by incandescent sodium glass, making it possible for workers to see clearly even into the heart of the flame. Some infrared absorption is also obtained by use of cerium and didymium. Additional information relative to the use of rare earths in optical glass is given in the footnote references^{35/} listed below.

The rare-earth oxides also may be used for tinting art glass, but this market depends somewhat upon the whims of fashion. Cerium glass typically has an attractive golden yellow color, but this may be due to a cerium-titanium combination. Neodymium is used to obtain a special type of purple glass of a peculiar characteristic color not obtainable with other materials. Praseodymium bestows a yellowish-green tint but is too rare and expensive for general use.

Cerium and neodymium are also said to be effective decolorizers in glass, although they have not been used commercially for this purpose in the United States. According to at least one authority (private communication) the virtue of cerium as a decolorizer depends upon its strong oxidizing properties. When cerium oxide is used it oxidizes the iron present to the ferric condition,

^{35/} Crookes, William, The Preparation of Eye-Preserving Glass for Spectacles: Phil. Trans. Roy. Soc., London, Ser. A, vol. 214, 1913, pp. 1-25.

Gibson, K. S. and Nicholas, H. J., The Ultraviolet and Visible Transmission of Eye-Protective Glasses: Nat. Bur. Standards Technol. Paper 119, 1918, 60 pp.

Taylor, William C. (to Corning Glass Works), Glass and Batch Therefor: U. S. Patents 1292147-8, Jan. 21, 1919.

in which condition it imparts more of a yellowish cast than green and with the cerium, cobalt is used to neutralize the yellow produced by the oxidizing effect of the cerium on the iron. Possibly the dissimilar results obtainable with cerium may be explained by the differing effects of cerous and ceric compounds.

Textile Treatment

A relatively new use for rare-earth mixtures is as a waterproofing agent and mildew preventive. It is said that treatment with these products provides protection against dampness for textiles (such as canvas fire hose or tents used in moist climates) that are subjected to an unusual amount of moisture.

The treatment of fabrics with aqueous solutions of casein and a salt of a rare-earth metal, such as cerium, thorium, or lanthanum, for mothproofing has been patented,³⁶ and filter-press cloths may be treated with cerium fluoride to protect them against the corrosive action of acid liquors and vapors.³⁷

Alloys

A new light alloy which has been given the name "ceralumin C", has been introduced in England by J. Stone & Co. This contains 0.15 percent cerium, 2.5 percent copper, 1.5 percent nickel, 0.8 percent magnesium, 1.2 percent iron, and 1.2 percent silicon. It is claimed that cerium refines the microstructure and suppresses the formation of the brittle iron-aluminum constituent.³⁸ Foreign patents have been issued for magnesium alloys, hardened by the addition of as much as 32 percent cerium or cerium metals, for internal-combustion engine pistons; stainless chromium-nickel steel alloys containing up to 10 percent rare-earth metals (or tantalum, columbium, or hafnium); and aluminum alloys containing up to 5 percent lanthanum (alone or in combination with other metals) for making motor pistons and cylinders.

Miscellaneous Uses

Numerous minor uses for cerium and other rare-earth metals have been developed, but they account for very small quantities of these materials and in general represent requirements that could be met as satisfactorily and usually more cheaply by other mineral substances. However, a few of them are worth noting, if only to demonstrate the diversified applications to which the rare earths are adapted. Cerium oxalate and other salts are used medicinally in the treatment of seasickness and nervous disorders. Cerium metal may be used in the laboratory for the reduction of columbium, tantalum,

³⁶/ Jones, Hilton Ira. Method of Mothproofing Fabrics: U.S. Patent 1638717, Oct. 23, 1928.

³⁷/ Mining Journal (London), Uncommon Metals: Vol. 180, no. 5086, Feb. 11, 1933, p. 15.

³⁸/ Chemical Industries, New Light Alloy: Vol. 35, no. 4, October 1934, p. 323.

etc., as a gas purifier in connection with the manufacture of neon lamps and as a "getter" material (when alloyed with iron, magnesium, or aluminum associated with a nitride and a suboxide of the rare-earth metals.^{39/}) The oxidizing action of cerium compounds has led to their use in photography, as oxidizing catalysts in organic preparations, and as an ingredient in "driers." Cerium salts have been employed in weighting silk and as mordants in dyeing cotton. As used in the dyeing and tanning of leather the hide decomposes the salts, fixing the cerium in the form of the hydrated oxide; it partly reduces the ceric sulphate or ceric ammonium nitrate, absorbing oxygen in the process, and yields a good quality of leather which has a yellow tint and resists the action of water. Ceric sulphate is used in volumetric analysis.

Yttrium is still more or less of a laboratory curiosity, but a glimpse of its potential usefulness is revealed by scanning the patent literature, which provides for fatty-acid salts of yttrium or other metals for use in the impregnation of textile materials as an insecticide; arc-lamp electrodes made from carbon with iron carbide and at least two carbides of metals "having complementary spectra rich in ultra-violet radiation such as *** yttrium carbides"; acid-resistant alloys comprising 8 to 12 parts yttrium, together with a similar proportion of uranium and larger quantities of tantalum and columbium; and a series of alloys said to exhibit selective radiation at luminous temperatures, which include yttrium and erbium, tantalum and yttrium, molybdenum and yttrium, zirconium and yttrium, and thorium and yttrium.

THE INDUSTRY IN THE UNITED STATES

No rare-earth minerals are mined in the United States except perhaps occasional specimens found at feldspar mines. The only natural raw material used commercially is monazite, all of which is imported, and the domestic industry starts with extraction of the rare earths from this mineral.

Deposits of monazite and other rare-earth minerals are scattered throughout the United States, but only in North and South Carolina, Idaho, and Florida has there been commercial production. Mining began in 1886 in the Brindletown district, Burke County, N. C., and the Carolina deposits accounted for the entire domestic output of monazite until 1903, when production began in Idaho. During the next 7 or 8 years these two States and South Carolina produced more or less regularly. Production ceased entirely from 1911 to 1914, inclusive, and was resumed on a small scale from 1915 through 1917 only. Subsequently the only output reported was a ton of monazite sand recovered in 1925 from a deposit 4 miles south of Jacksonville Beach, Fla.

^{39/} Miller, Henry (New Process Metals Corporation), Degasifying Devices Such as Thermionic Tubes: U.S. Patent 1864084, June 21, 1932.

During the 10-year period 1900 to 1909 inclusive, when the domestic industry was at its height, the cost of producing monazite in the United States was considerably higher than the cost of importing it from Brazil. The cost of producing 1 ton of domestic concentrates containing 92 to 95 percent monazite was estimated to be approximately \$169 at the concentrating plant, whereas Brazilian monazite was laid down at German ports at prices ranging from \$95 to \$120 per ton (5 percent thorium), a difference of \$45 to \$70 per short ton. When the Indian monazite first came on the market in 1911 American monazite cost approximately \$260 per ton, and Brazilian monazite was being sold on the world markets at approximately \$133 per ton. Indian monazite, however, was exported at a price ranging from \$120 to \$126, or about one half that of the American product, and it carried over 50 percent more thorium (ThO_2) than the American monazite.

Although there was still monazite sand in the United States it could not be produced in competition with foreign monazite, and the industry was forced to close. Even the Brazilian monazite, which is richer in thorium than the American monazite, found competition with the still richer Travancore monazite very difficult. Further declines in price to \$50 a ton merely have intensified the situation. Moreover, the relatively low thorium content of monazite produced in the United States has proved an additional handicap in competing with material imported from Brazil and India.

Figures for the production of monazite in the United States from 1893 to 1925 will be found in the world production table on page 35.

No means are available for estimating the extent of the rare-earth industry in the United States. According to the Bureau of the Census, the domestic production of cerium compounds was valued at \$239,690 in 1929 and at \$403,730 in 1931. No figures are available for 1933, as there were only two producers in that year. The only other index of consumption of cerium products is in the manufacture of incandescent mantles. These figures are given in terms of values, which mean little with respect to the quantity of cerium consumed. Five manufacturers of gas mantles reported production in 1933 - 1 each in Illinois, Kansas, Missouri, New Jersey, and New York.

Pyrophoric alloys are manufactured by only one firm in the United States, consequently no production figures are available.

Late in 1934 the American Treibach Chemical Works, Inc., manufacturer of metallic cerium and products of the rare-metal fields, established a branch plant at Niagara Falls, N.Y. The raw material is purchased cerium chloride. According to published report^{40/} the plant is to serve as an experimental work for the Treibacher Chemisch Works of Treibach, Austria.

^{40/} Chemical Industries, New Cerium Source: Vol. 34, no. 5, May 1934, pp. 450-451.

IMPORTS

Before 1909 imports of monazite into the United States were negligible. In that year 35 tons of monazite valued at \$8,324 were brought in, and subsequently imports increased more or less steadily, reaching a peak of 2,914 short tons valued at \$355,017 in 1917. In general, however, shipments to the United States are erratic and may jump from a fraction of a ton in one year to 1,500 tons or more in the following year. In 1933 and 1934 imports amounted to only 56 short tons and 112 short tons, respectively. Imports of monazite from 1909 to 1934 are shown in the following table.

TABLE 3. - Monazite sand imported for consumption
in the United States, 1909-34^{1/}

Year	Short tons	Value	Unit value	Year	Short tons	Value	Unit value
1909	35	\$8,324	\$238	1922	1,733	\$210,187	\$121
1910	227	39,699	175	1923	127	11,334	89
1911	353	60,542	171	1924	273	13,320	67
1912	278	47,334	170	1925	---	---	---
1913	409	65,848	161	1926	335	23,816	71
1914	385	61,595	160	1927	597	41,029	69
1915	937	161,456	172	1928	442	24,151	55
1916	1,218	188,383	155	1929	577	26,114	45
1917	2,914	355,017	122	1930	---	---	---
1918	1,497	204,661	137	1931	1,698	65,080	38
1919	316	48,768	154	1932	1,569	48,639	31
1920	907	141,528	156	1933	56	1,935	35
1921	(2/)	40	-	1934	112	4,867	43

^{1/} Bureau of Mines, Mineral Resources of the United States; and Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation of the United States.

^{2/} 50 pounds.

Imports of cerium metal, ferrocerium, and various cerium salts have been reported separately only since 1922. After the passage of the Tariff Act of 1930 imports of cerium fluoride and cerium nitrate were reported together, but in recent years the quantities of these salts and other cerium compounds shipped into the United States from abroad have dwindled to insignificant proportions. Imports from 1922 to 1934, inclusive, are given in the following tables.

TABLE 4. - Imports of cerium metal and of ferrocerium and other cerium alloys, 1922-34^{1/}

Year	Cerium metal			Ferrocerium and other alloys		
	Pounds	Value	Unit value	Pounds	Value	Unit value
1922 ^{2/}	---	---	---	---	---	---
1923	38	\$1,031	\$27.15	---	---	---
1924	---	---	---	100	\$208	\$2.08
1925	4	16	4.00	89	185	2.08
1926	20	196	9.80	1	22	22.00
1927	5	35	7.00	71	118	1.66
1928	16	57	3.56	2,085	5,999	2.88
1929	---	---	---	2,524	6,931	2.75
1930	4	13	3.25	861	2,824	3.28
1931	---	---	---	---	---	---
1932	---	---	---	---	---	---
1933	---	---	---	44	232	5.27
1934	---	---	---	---	---	---

1/ U.S. Tariff Commission, Summary of Tariff Information: Sched. 3, 1929, p. 624; Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation of the United States.

2/ Sept. 22 to Dec. 31, 1922.

I. C. 6847.

TABLE 5. - Imports of cerium nitrate, cerium fluoride,
and other cerium salts, 1922-34

Year	Cerium nitrate			Cerium fluoride			Other cerium salts, not specially provided for		
	Pounds	Value	Unit value	Pounds	Value	Unit value	Pounds	Value	Unit value
1922 ^{1/}	---	---	---	54	\$ 25	\$ 0.46	3	\$ 24	\$8.00
1923	1,007	\$866	\$0.86	38,971	3,058	.08	4,821	746	.15
1924	2,258	2,410	1.07	36,650	1,173	.03	83,581	4,361	.05
1925	5,124	5,535	1.08	---	---	---	16,969	1,487	.09
1926	124	181	1.46	---	---	---	11,503	894	.08
1927	20	34	1.70	39,683	2,469	.06	47,155	3,627	.08
1928	102	121	1.18	100	26	.26	100,624	8,047	.08
1929	50	82	1.64	---	---	---	133,935	10,165	.08
1930	3/16	3/9	.56	4/156	4/240	1.54	87,948	13,204	.15
1931	---	---	---	---	---	---	397	44	.11
1932	---	---	---	---	---	---	---	---	---
1933	---	---	---	---	---	---	---	---	---
1934	---	---	---	---	---	---	---	---	---

^{1/} U.S. Tariff Commission, Summary of Tariff Information, Sched. 1, 1929, p. 410; and Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation of the United States.

^{2/} Sept. 22 to Dec. 31, 1922.

^{3/} Jan. 1 to June 17, 1930.

^{4/} June 18 to Dec. 31, 1930. Cerium nitrate and cerium fluoride grouped together.

TARIFF

The Tariff Act of 1930 makes the following provisions for rare-earth ores and products:

Provisions of Tariff Act of 1930 for rare earths

Para-graph	Tariff classification	Rates of duty specified and ad valorem
1721	Monazite sand and other thorium ores	Free.
1644	Cerite or cerium ore	Free.
302(p)	Cerium metal	\$2 per pound.
302(q)	Ferrocium and all other cerium alloys	\$2 per pound and 25 percent ad valorem.
1534	Gas, kerosene, or alcohol mantles and mantles not specially provided for, treated with chemicals or metallic oxides, wholly or partly manufactured	40 percent ad valorem.
87	Thorium nitrate, thorium oxide, and other salts of thorium not specially provided for, also gas-mantle scrap consisting in chief value of metallic oxides	35 percent ad valorem.

The foregoing provisions are identical with those in the Tariff Act of 1922. However, the 1922 act provided, under paragraph 1577, for "flint, flints, and flint stones, unground" on the free list. As the small pieces of pyrophoric alloy used in pocket lighters and gas lighters were commercially known as flints, importations of these items were held free of duty under paragraph 1577 of the 1922 act rather than dutiable under the provision in the Metals Schedule for "ferrocium and all other cerium alloys" at \$2 per pound and 25 percent ad valorem (Treasury Decision 42686). A rehearing subsequently was granted (Abstract (N) 5838), and pending final decision the Treasury Department issued instructions (C.I.E. 1172) that such flints be classified as dutiable. This ambiguity was removed in writing the Tariff Act of 1930, the provision on the free list being altered to read "natural flints and flint stones."

Before the act of 1922 monazite sand and thorite were dutiable, the rate under the 1913 act being 25 percent of the foreign market value compared with 4 cents per pound under the 1909 act and 6 cents per pound under the act of 1897. "Cerium, cerite, or cerium ore", however, were specifically provided for on the free list of the acts of 1909 and 1913, and under the earlier acts "cerium" was admitted free of duty.

EXPORTS

In the brief period before the discovery of the richer Brazilian deposits, the United States was the leading producer of monazite, supplying not only our own market but substantially all that was consumed in the thorium nitrate industry in Europe. Although no figures are recorded it is understood that from one fourth to one third of the domestic production of monazite sand was exported annually to England and Germany and there used for the manufacture of thorium salts, principally nitrate. However, an export trade could not be maintained against the plentiful supply of cheaper and richer monazite which began to come from Brazil in 1895 and which eventually stifled even the home trade in domestic monazite.

A table of exports of incandescent gas mantles will be found on page 24.

THE INDUSTRY IN FOREIGN COUNTRIES

Monazite production

Prior to the development in 1911 of a monazite-mining industry in India, Brazil was the leading foreign source of supply. The thoria content of high-grade Brazilian monazite concentrates is about 6 percent, which is somewhat lower than that of the Indian ore, although high enough to eliminate the United States as a monazite-producing country. As the market for monazite has been regulated largely by the demand for thoria (for use in incandescent mantles), Indian monazite has tended to supplant the Brazilian product. The decline of the mantle industry and the development of additional outlets for cerium may partly offset this preference, particularly as the ceria and mixed rare-earth contents of Brazilian monazite apparently are as high as in the ore from India.

Brazil. - The mining of monazite sand was begun in Brazil by an American, John Gordon, who realized a considerable profit by shipping the product to Germany as ballast. In 1903 the Brazilian Government decided that the deposits of this mineral along the seacoast belonged to the State and forbade their free exploitation. Bids were let, and the A.C. de Freytas Co., of Hamburg, obtain the rights to exploit these deposits, but later the company formed a partnership with John Gordon, the original shipper of this mineral. They sold their entire output to the German thorium syndicate and in this manner held a partial monopoly over the production of monazite in Brazil.

It was soon found that other manufacturers of thorium products were able to obtain supplies elsewhere and that the whole output from Brazil could not be controlled, so the German syndicate decided to eliminate all competition. Accordingly, in January 1906 the price of thorium nitrate was reduced nearly one half. Sales were made only to consumers, and each consumer was permitted to buy only such quantities as he expected to require for his own needs with no surplus for resale.

The result of this cut in price was to eliminate the smaller manufacturers of thorium nitrate. Although it had little effect upon the larger well-established firms mining their own monazite, the formation of this cartel and the reduction in the price of thorium nitrate had considerable bearing on the export trade of monazite from Brazil. Before 1903 the exports never exceeded 3,400 short tons annually, but after that date the export trade in this mineral increased rapidly until in 1909 it reached its peak - 7,121 tons valued at \$704,387. By 1912 Indian monazite, with its higher thoria content, had entered the world market, and exports from Brazil declined. This downward trend has continued, and since 1920 shipments have been less than 500 tons annually.

When the exports of monazite sand were at their peak it was estimated that Germany took about two thirds of the total, the balance going to France, the United States, and England, in amounts that decreased in the order named. In 1926 the United States took almost all of the monazite exported from Brazil; in 1927 and 1928 Germany was the sole purchaser and in 1929 took all but a few tons, which went to the United States; and in 1930 exports, amounting to only 15 metric tons, were shipped to the Netherlands. Information is not available as to the destinations of subsequent shipments.

India. - Monazite from Travancore, India, first appeared on the world markets in 1911, when exports of 932 short tons valued at \$117,010 were reported officially. Shipments increased during the next few years, reaching a peak of 2,371 short tons valued at \$286,243 in 1918. From 1919 to 1930 exports dropped off considerably, probably as a result of the decline in the gas-mantle trade, but in 1931 (year ended July 31) more than 1,500 short tons of monazite were exported, and subsequent shipments have been unusually heavy. Within the last 3 or 4 years virtually all the monazite imported into the United States has been obtained from India.

Before the World War the monazite output, which was obtained from beach sands between Muttum and Colachel in Travancore, was in the hands of a firm operated under German control. After the outbreak of the war this German interest was soon eliminated, and the industry was placed under the control of British capital. The deposits are worked by Travancore Minerals Co., Ltd., affiliated with Thorium, Ltd., of London, manufacturer of thorium products.

According to available statistics no distinction appears to have been made between production and exports of monazite sand from Travancore before 1919. Exports for later years have been reported as follows:

TABLE 6. - Monazite sand exported from Travancore, India, 1919-33^{1/}

Year	Quantity (short tons)	Year	Quantity (short tons)
1919	---	1927	563
1920	1,053	1928	90
1921	---	1929	349
1922	22	1930	---
1923	230	1931	2/1,565
1924	112	1932	2/1,979
1925	319	1933	2/909
1926	388		

1/ Imperial Institute Statistical Summaries, 1919-33.

2/ Year ended July 31.

TABLE 7. - World production of monazite sand, 1893-1933, (in short tons)^{1/}

r	United States	Brazil ^{2/}	India	Ceylon	Total	United States percent of total
3	65	- - -	- - -	- - -	65	100
4	273	- - -	- - -	- - -	273	100
5	787	3,307	- - -	- - -	4,094	19
6	15	192	- - -	- - -	207	7
7	22	249	- - -	- - -	271	8
8	125	2,149	- - -	- - -	2,274	5
9	175	2,932	- - -	- - -	3,107	6
0	454	1,633	- - -	- - -	2,087	22
1	374	1,811	- - -	- - -	2,185	17
2	401	1,328	- - -	- - -	1,729	23
3	431	3,636	- - -	- - -	4,067	11
4	372	5,357	- - -	- - -	5,729	6
5	672	4,891	- - -	- - -	5,563	12
6	423	4,797	- - -	- - -	5,220	8
7	274	4,891	- - -	- - -	5,165	5
8	211	5,473	- - -	- - -	5,684	4
9	271	7,121	- - -	- - -	7,392	4
0	50	5,994	- - -	- - -	6,043	(3/)
1	- -	4,064	932	- - -	4,996	- -
2	- -	3,746	1,271	- - -	5,018	- -
3	- -	1,584	1,383	- - -	2,967	- -
4	- -	661	1,323	- - -	1,989	- -
5	18	484	1,241	- - -	1,743	1
6	19	- - -	1,448	- - -	1,467	1
7	11	1,252	2,173	- - -	3,436	(3/)
8	- -	551	2,371	22	2,944	- -
9	- -	161	2,267	- - -	2,428	- -
0	- -	1,270	1,838	81	3,189	- -
1	- -	366	1,411	84	1,861	- -
2	- -	127	140	112	379	- -
3	- -	- - -	276	- - -	276	- -
4	- -	- - -	697	2/28	725	- -
5	1	22	.05	- - -	198	(3/)
6	- -	221	72	- - -	293	- -
7	- -	224	314	4/155	693	- -
8	- -	112	116	4/112	340	- -
9	- -	99	202	4/ 85	386	- -
0	- -	17	16	- - -	33	- -
1	- -	- - -	100	- - -	100	- -
2	- -	330	733	- - -	1,063	- -
3	- -	449	- - -	- - -	449	- -

Figures compiled from various official sources.

Exports.

Less than 1 percent.

Exports (Mining Jour., London, vol. 171, no. 4970, Nov. 22, 1930, p. 913).

Ceylon. - Production of monazite was undertaken in Ceylon in 1918, when 22 short tons were recovered as a byproduct of gem washing. During the next 10 years fairly substantial shipments were reported, but discrepancies^{41/} in available statistics make it difficult to determine the importance of Ceylon as a source of monazite. The thorium content apparently is comparable with that of Indian monazite, and the Government of Ceylon, with the assistance of the Imperial Institute, established monazite works at Induruwa, a few miles from Colombo; however, difficulty was experienced in disposing of the monazite sand recovered, and in the latter part of 1927 it was proposed to abandon the works.

Available statistics covering world production of monazite from 1893 to 1933, inclusive, are given in table 7.

Rare-Earth Products

Outside of the United States the leading producers of rare-earth products are in Berlin, Paris, and London. In 1930 Deutsche Gasglulicht Auer G. M.b.H., Berlin; Sté. Minière & Industrielle Franco-Bresilienne and Sté. de Produits Chimiques des Terres Rares, both of Paris; and Thorium, Ltd., of London, entered into an agreement^{43/} with the Lindsay Light Co. of Chicago, Ill., for the apportionment of world markets for monazite and its derivatives (other than ferrocerium). Under the terms of this agreement the Lindsay Light Co. was required to restrict its sales to the United States and Canada, and the European firms were bound to refrain from exporting thorium or any product derived from monazite sand, except ferrocerium, to the United States. This contract became effective April 9, 1930 and was to continue in effect until March 31, 1940. A further agreement was made between the Lindsay Light Co. and the Travancore Minerals Co., Ltd., under the terms of which the latter company was to furnish monazite to no other firms in the United States than the Lindsay Light Co., this agreement to remain in effect from September 1, 1931 to August 31, 1934. However, on March 5, 1934 the United States Federal Trade Commission ordered^{44/} that the Lindsay Light Co. cease and desist from carrying out the terms of the aforementioned contracts and refrain from entering into new agreements of a similar nature.

Germany. - Germany is an important factor in world trade in rare earths, as indicated by the following table covering exports of thorium, cerium, and radium salts from that country.

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- 41/ Exports equivalent to 155 short tons, 112 short tons, and 85 short tons in 1927, 1928, and 1929, respectively, mentioned in Mining Jour. (London), vol. 171, no. 4970, Nov. 22, 1930, p. 913, do not appear in Imperial Inst. Statistical Summary covering those years, although exports amounting to 85 long tons in 1928 are recorded.
- 42/ Mining Journal (London), Ceylon Monazite Works to be Closed Down: Vol. 158, Sept. 10, 1927, p. 760.
- 43/ Federal Trade Commission, Complaint, in the Matter of Lindsay Light Co.: Docket 2142, Dec. 22, 1933, 5 pp.
- 44/ Federal Trade Commission, Order to Cease and Desist, In the Matter of Lindsay Light Co.: Docket 2142, Mar. 5, 1934, 3 pp.

TABLE 8. - Exports of rare earths and their compounds (thorium, cerium, and radium salts, etc.) from Germany, 1927-34

Year	Quantity, metric tons	Value, RM
1927	57.03	619,000
1929	140.15	768,000
1930	75.45	494,000
1931	63.69	402,000
1932	66.01	308,000
1933	83.98	380,000
1934	114.3	377,000

In 1927 the United States was the leading purchaser of German rare-earth products, with the United Kingdom, Japan, and the U.S.S.R. following in decreasing order of importance. In 1929 considerably more than one third of the German exports of rare earths went to the United States, and substantial quantities were shipped to Austria, the United Kingdom, and Japan. Subsequently, Austria and the U.S.S.R. have been the principal markets for German exports; no shipments to the United States have been reported since 1930, and Great Britain's purchases have dropped to inconsequential proportions. Germany's imports of monazite, which amounted to only 2 tons and 1 ton, respectively, in 1932 and 1933, increased to 325 metric tons in 1934. In 1929 ore supplies were obtained almost entirely from Brazil, but this source has been superseded by India. Figures covering world production of gas mantles are not available, but on the basis of exports Germany is by far the leading producer. Exports amounted to 75,514 gross in 1931, 61,313 gross in 1932, and 56,389 gross in 1933.

France. - Little information is available with respect to the rare-earth industry in France. Exports of thorium nitrate and other rare-earth salts amounted to only 193 cwt. in 1931, 614 cwt. in 1932, and 498 cwt. in 1933. France ranks fourth in exports of gas mantles. The rare-earth industry in France is controlled by two firms, one of which has Brazilian connections.

Great Britain. - The leading British producer of rare-earth products is Thorium, Ltd., an affiliate of Travancore Minerals, Inc. In recent years imports of monazite (usually amounting to 150 to 250 long tons) have been obtained almost entirely from British India. Exports of rare earths are not available, but gas mantles are exported in considerably greater quantity (19,733 gross in 1933) than from the United States. Gas mantles also are imported; figures for recent years are 13,874 gross in 1931, 1538 gross in 1932, and 555 gross in 1933. Imports of rare-earth compounds are shown in the following table:

TABLE 9. - Rare-earth compounds imported into the United Kingdom, 1929-33^{1/}

Year	Cerium fluoride and other fluorides		Other salts (except ThNO ₃)		Approximate total value
	Pounds	Value	Pounds	Value	
1929	18,666	£1,749	4,628	£ 879	2,600
1930	7,159	621	2,080	705	1,300
1931	10,183	911	2,779	1,516	2,400
1932	350	54	665	333	400
1933	134	18	1,553	568	600

^{1/} Trade of the United Kingdom (annual).

Thorium, cerium, and other rare-earth metals (but not the ores and minerals) are dutiable^{45/} at 33 1/3 percentum ad valorem under the Safeguarding of (Key) Industries Act of 1921. The act originally in force for 5 years, was extended to 1936. Goods from other parts of the Empire may be brought in free if 25 percent of the value has been acquired in the Empire.

MARKETS AND PRICES

Virtually the only available barometer of the rare-earth industries is the demand for monazite. In the past monazite has been valued chiefly for its thorium content, and for many years during the heyday of gas-mantle manufacture relatively large stocks of residues were accumulating, from which only a small fraction of the cerium metals was extracted, along with the thorium. As these stocks tend to be absorbed for making pyrophoric alloys and other purposes, the trend is toward a demand for monazite for its cerium content. Under these circumstances the Carolina monazite would not be classed as inferior to the Brazilian or Indian product and might eventually command a premium because of its high rare-earth content. It remains to be seen, however, whether the premium could offset the much lower cost of production in Travancore, where labor is so cheap and where the monazite has become essentially a byproduct of the greatly expanded production of ilmenite for making titanium pigments. It is likely that an increased demand for monazite might actually reduce the price by providing an incentive for a better recovery from the rejects of ilmenite production and distributing costs over a larger tonnage.

The price of monazite sand has fluctuated considerably since the World War, in most instances reflecting the declining use of the mineral. During the war the price of monazite sand delivered in New York, exclusive of the duty of 25 percent, ranged from \$25 to \$40 per unit (20 pounds, or 1 percent of a short ton), or \$150 to \$240 per ton, based on 6 percent thoria content. Shortly after the war the price was quoted (November 1919) at \$27 per unit, or about \$162 per ton of the 6-percent (thoria) sand, duty not paid.

^{45/} Pratt, J. Davidson, *Tariffs in the Chemical Industry: Chem. and Ind.*, vol. 53, July 6, 1934, p. 583.

Before the end of 1925 the price had dropped to \$120 per short ton (6 percent ThO_2). After increasing slightly during the latter part of 1928 to \$130 per ton, the price fell to \$60 a ton during the late fall of 1929 and continued at this level until the middle of 1932. The slightly increased quotation (\$63) which then became effective was based upon a minimum thorium content of 8 percent. In June 1933 the price dropped to \$50 per ton - the lowest quotation so far recorded in the history of the industry - and remained there until May 1934, when it returned to \$60 per ton, the present level.

Quotations for monazite sand at New York, 1920 to 1934, inclusive, are shown in the following table:

TABLE 10. - Prices of monazite, 1920-34 (per short ton, minimum 8 percent thorium)^{1/}

Year	High	Low	Year	High	Low
1920	\$252	\$180	1928	\$130	\$120
1921	180	180	1929	130	60
1922	180	120	1930	60	60
1923	160	120	1931	60	60
1924	160	120	1932	63	60
1925	160	120	1933	63	50
1926	120	120	1934	60	50
1927	120	120			

^{1/} Engineering and Mining Journal, Minimum 6 percent ThO_2 prior to July 1932.

Published quotations are not available for most of the rare-earth products, although prices for small lots may be obtained upon request from chemical manufacturers and mineral dealers.

Cerium hydrate is currently (April 1935) quoted at 75 cents per pound, in drums, f.o.b. sellers' works, and prices for the oxalate are 28 cents per pound, in 300-pound barrels, or 30 cents per pound in 100-pound kegs.

TRADE LISTS

Producers and DealersMonazite and other rare-earth minerals:

Industrial Minerals Corporation, 220 Delaware Avenue, Buffalo, N.Y.
(monazite & samarskite).
O. P. Babbitt, 281 Molino Street, Long Beach, Calif. (monazite).
Golwynne Magnesite & Magnesia Corporation, 1532 Chrysler Bldg., New
York City (Indian monazite).
Foote Mineral Co., 1610 Summer Street, Philadelphia, Pa.
Charles Mohr, Crisman Star Route, Boulder, Colo. (cerite).
L. B. Perkins, Marion, Va. (allanite).
Bradley Johnson, Penland, N. C. (allanite).
Emerald Park Mining & Development Co., Box 374, Buffalo, Wyo. (allanite).

Cerium metal and compounds:

Lindsay-Light Co., Chicago, Ill. (hydrate, nitrate, and oxide).
Maywood Chemical Works, Maywood, N.J. (salts).
Wolff-Alport Chemical Corporation, 1127 Irving Avenue, Brooklyn, N.Y.
(hydrate).
Harrison Manufacturing Co., Rahway, N.J. (salts).
Vitro Manufacturing Co., Corliss Station, Pittsburgh, Pa. (hydrate and
oxide).
New Process Metals Corporation, 46 Center Street, Newark, N.J. (ferrocenium).
E.I. du Pont de Nemours & Co., Inc. (R. & H. Chemicals Dept.), 11th and
Orange Streets, Wilmington, Del. (hydrate).
Belmont Smelting & Refining Works, Inc., 320 Belmont Avenue, Brooklyn,
N.Y. (metal).
R.T. Vanderbilt Co., Inc., 230 Park Avenue, New York, N.Y. (oxide).
Foote Mineral Co., 1610 Summer Street, Philadelphia, Pa. (carbonate,
nitrate).
Mallinckrodt Chemical Works, Second and Mallinckrodt Streets, St. Louis, Mo.
(nitrate and oxalate).
Merck & Co., Inc., 1935 Kerrigan Road, Rahway, N.J.
Frederick G. Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio.
(nitrate and sulphate).
American Treibach Co., 522 Fifth Ave., New York, N.Y. (cerium metal -
plant at Niagara Falls, N.Y.)

Gas Mantles:

Lindsay-Light Co., Chicago, Ill.
Welsbach Co., Gloucester City, N.J.
Coleman Lamp & Stove Co., Wichita, Kans.
General Gas Mantle Co., Camden, N.J.
Erie Manufacturing Co., Erie, Pa.

Possible BuyersIonazite:

Lindsay-Light Co., Chicago, Ill.
Maywood Chemical Works, Maywood, N.J.
Harrison Manufacturing Co., Rahway, N.J.
A. D. Mackay, 198 Broadway, New York, N.Y.
The Harshaw Chemical Co. of New York, 150 Nassau Street, New York, N.Y.
Varlacoid Chemical Co., 15 Moore Street, New York, N.Y.
National Jewelry & Importing Co., 104 King Street, Winnipeg, Canada.
Blackwell's Metallurgical Works, Ltd., Speke Road Works, Garston,
Liverpool, England.

Cerium and other rare-earth compounds:

Varlacoid Chemical Co., 15 Moore Street, New York, N.Y.
A. D. Mackay, 198 Broadway, New York, N.Y.
The Harshaw Chemical Co. of New York, 150 Nassau Street, New York, N.Y.
Welsbach Co., Gloucester City, N.J.
Corning Glass Works, Corning, N.Y.
Pittsburgh Plate Glass Co., 2222 Grant Building, Pittsburgh, Pa.
National Jewelry & Importing Co., 104 King Street, Winnipeg, Canada.

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